

In Situ Observation of Nano-Oxide Formation in Magnetic Thin Films

Andrew T. McCallum and Stephen E. Russek

Abstract—*In situ* conductance and reflected high-energy electron diffraction (RHEED) measurements were taken during the oxidation of 20-nm-thick Co and CoFe layers. The conductance shows an initial drop with exposure to oxygen followed by a period of increasing conductance. This increase in conductance clearly indicates an increase in specular reflection of electrons at the oxide interfaces. The amount of conductance increase varied with deposition conditions. The sample with the highest increase in conductance showed an increase of $6.4 \times 10^{-4} \Omega^{-1}$ greater than the bare metal at 1.5×10^{-3} Pa·s of oxygen exposure. This corresponds to a minimum increase in the specularity of 0.05. RHEED measurements show a blurring of the face centered cubic (fcc) (111) texture with exposure to oxygen, indicating the formation of an amorphous oxide during the initial conductance drop and conductance increase. After the conductance begins to fall again, a new diffraction pattern appears in the RHEED data, indicating the formation of CoO with an fcc (111) texture but with a different lattice spacing.

Index Terms—Co, giant magnetoresistance, oxide layers, specularity.

I. INTRODUCTION

COMPUTER hard disk drives with larger data densities require spin valve read heads with higher giant magnetoresistance ratios. One of the most promising ways to increase the magnetoresistance of a spin valve is to increase the specular reflection at the interfaces. Use of NiO as the capping and anti-ferromagnetic layers in spin valves has been shown to increase the giant magnetoresistance (GMR) in this manner [1]–[3]. Spin valves using NiO or Fe₂O₃ are not useful for device applications due to small exchange bias, thermal instability, and hard magnetic properties [4].

Another approach to creating specular interfaces is to oxidize part of the free and pinned ferromagnetic layers, creating a nano-oxide layer [4]–[6]. Spin valves with thin oxide layers included have been shown to have GMR ratios of up to 20% [4]. In the simplest free electron model of the electron transport in a spin valve, adding completely reflecting layers outside of the ferromagnetic layers would make a trilayer behave like a superlattice with a much larger giant magnetoresistance [1]. Knowledge of the oxidation process may yield ways to increase the specularity of the oxide interfaces and produce spin valves with larger magnetoresistance.

II. EXPERIMENT

In situ conductance measurements provide a useful tool for studying the oxidation of metal surfaces. A four-probe van der Pauw technique was used to measure the conductance once per second during deposition and oxidation of ferromagnetic samples [7], [8]. The change in conductance due to a monolayer of metal being deposited or oxidized is much larger than the minimum measurement sensitivity of $1.5 \times 10^{-5} \Omega^{-1}$. At a pressure in the range of 10^{-6} Pa, several minutes are required for a monolayer of oxygen to impact the surface, providing ample time for many conductance measurements to be made. This allows for detailed observation of the oxidation process. *In situ* reflected high-energy electron diffraction (RHEED) measurements provide a useful complement to the conductance measurements. The RHEED data yields information on the crystal structure, orientation, roughness, and quality of the surface.

The samples used consisted of Ta(5 nm) – Ni_{0.8}Fe_{0.2}(5 nm) – Co(20 nm) or Ta(5 nm) – Ni_{0.8}Fe_{0.2}(5 nm) – Co_{0.9}Fe_{0.1}(20 nm). The samples were sputter deposited at a pressure of 0.5 Pa on oxidized silicon substrates. The base pressure of the system was less than 10^{-6} Pa. The Ta and Ni_{0.8}Fe_{0.2} are the seed layers that set up the uniform coverage and fcc (111) texture. Although the equilibrium structure of Co is hexagonal close packed (hcp), the Co deposited on the Ni_{0.8}Fe_{0.2} retained an fcc structure.

More than one electron mean free path separates the bottom surface of the Co from the top surface. This effectively isolates the current density near the top surface from any effects of the bottom surface. In this regime, the Boltzmann transport equation can be solved analytically for the changes in conductivity due to oxidation:

$$\Delta G = \sigma \Delta t + \frac{3}{16} \sigma_{\uparrow} \lambda_{\uparrow} \Delta p_{\uparrow} + \frac{3}{16} \sigma_{\downarrow} \lambda_{\downarrow} \Delta p_{\downarrow} \quad (1)$$

where ΔG is the change in conductance, σ is the conductivity of the material deposited, Δt is the change in the thickness of the layer, σ_{\uparrow} and σ_{\downarrow} are the conductivities due to majority and minority electrons, λ_{\uparrow} and λ_{\downarrow} are the mean free paths for majority and minority electrons, and Δp_{\uparrow} and Δp_{\downarrow} are the changes in specular scattering probabilities for the majority and minority electrons at the top surface [8]. The conductivity can be measured directly from the slope of the conductance as a function of thickness. The spin-dependent electron mean free paths are proportional to the spin-dependant conductivities with a proportionality coefficient of $1.8 \times 10^3 \Omega \text{nm}^2$ [8], [9]. Since the majority conductivity is ten times larger than the minority conductivity and the spin-dependent electron mean free paths are proportional to the conductivities, then the total possible amount

Manuscript received October 15, 2003.

The authors are with the National Institute of Standards and Technology, Boulder, CO 80305 USA (e-mail: mccallum@boulder.nist.gov; russek@boulder.nist.gov).

Digital Object Identifier 10.1109/TMAG.2004.829170

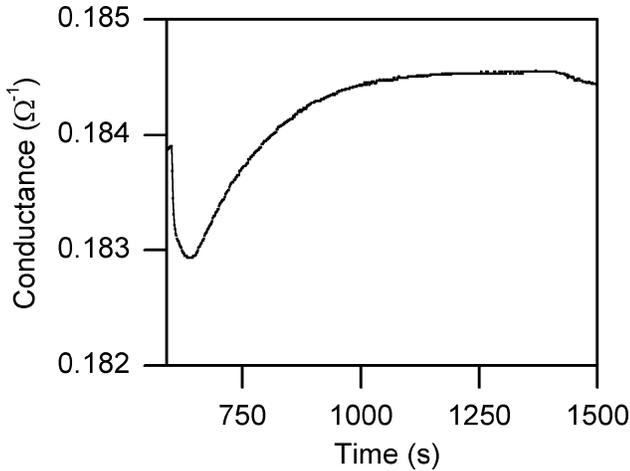


Fig. 1. Conductance as a function of time for a Ta(5 nm) – Ni_{0.8}Fe_{0.2}(5 nm) – Co_{0.9}Fe_{0.1}(20 nm) sample after deposition with exposure to oxygen. The increase in the value of the conductance clearly indicates an increase in the specularity of the metal surface. The oxygen pressure did not exceed 8×10^{-6} Pa.

of change in conductance due to changes in the majority specular scattering probability $(3/16)\sigma_{\uparrow}\lambda_{\uparrow}$ will be 100 times the total possible amount of change in conductance due to changes in the minority specular scattering probability $(3/16)\sigma_{\downarrow}\lambda_{\downarrow}$ [8]. Changes in minority specular scattering probability will be ignored in this paper, due to its negligible effect.

Neglecting the minority spin electrons leaves the change in thickness of the layer and the change in the majority specular scattering probability as unknown quantities. During oxidation, the thickness of the Co layer will drop; therefore, any conductance increase must be due to increased specularity. Calculating the increase in specularity as though there were no change in thickness gives a lower bound to the specularity increase for any given conductance increase:

$$\Delta p_{\uparrow, \min} = \frac{16\Delta G}{3\sigma_{\uparrow}\lambda_{\uparrow}}. \quad (2)$$

III. RESULTS

When a bare Co_{0.9}Fe_{0.1} surface is exposed to oxygen, the conductance is reduced, as is seen in Fig. 1. The oxygen pressure did not exceed 8×10^{-6} Pa. The bare metal is expected to absorb oxygen at a higher rate than an oxidized surface; therefore, the relative speed of this drop is not surprising. Part of this drop in conductance may be due to a drop in specularity. Isolated oxygen atoms incorporated into the metal surface may be acting as scattering centers, lowering the specularity. After quickly falling, the conductance reaches a minimum value at 5×10^{-5} Pa·s of oxygen exposure. Then, the conductance rises to a level greater than that of the bare metal, indicating an increase in specularity. A minimum specularity increase of 0.05 is calculated using (2) for the positive change in conductance between the bare metal and the maximum value seen during oxidation. After rising to this maximum value, at 1.5×10^{-3} Pa·s, the conductance begins to fall again. This is consistent with the specularity approaching some final value while the metal layer continues to thin, thus reducing the conductance. The rate at

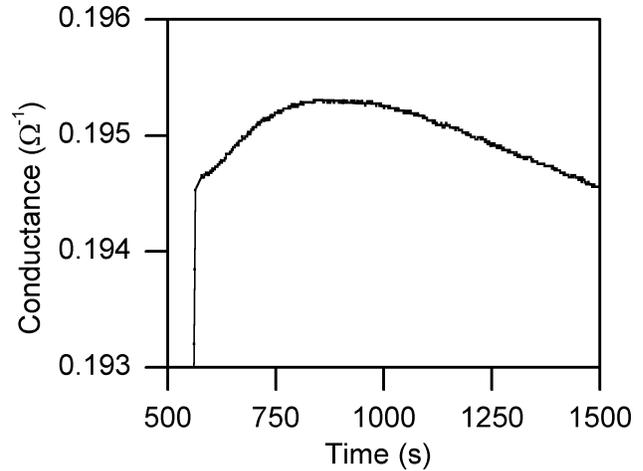


Fig. 2. Conductance as a function of time for a Ta(5 nm) – Ni_{0.8}Fe_{0.2}(5 nm) – Co_{0.9}Fe_{0.1}(20 nm) sample after deposition with no exposure to oxygen. This initial increase in conductance shows that the sample is self annealing at room temperature. The rearrangement of atoms in the surface may be a significant part of the behavior of the conductance during oxygen exposure.

which this final reduction in conductance occurs slows with further oxygen exposure. The thicker the oxide layer gets, the more it will prevent the oxygen absorbed on the oxide surface from quickly coming into contact with the Co atoms in the metal.

It is important to note that Co_{0.9}Fe_{0.1} and Co surfaces will self-anneal at room temperature, as seen in Fig. 2. Chemical rearrangement of the metal and the oxide surfaces may account for some of the behavior of the conductance as a function of time during oxygen exposure. In addition, the self-annealing might explain the variation between different samples. The flow of oxygen into the chamber was precisely controlled. However, this did not lead to precise control of the partial pressure of oxygen in the chamber since the chamber walls absorbed differing amounts of oxygen, depending on what had been deposited and how much oxygen had flowed into the chamber. If the self-annealing occurred at the same rate and if the sample were exposed to a different partial pressure of oxygen, then the conductance behavior would be different.

Fig. 3(e) shows the conductance as a function of time for a Co sample with pauses between oxygen doses. The oxygen flow was paused in order to allow RHEED pictures to be taken. Although the conductance is clearly affected by the self-annealing occurring during periods without oxygen, the pattern of conductance drops and increases is still the same. The initial period of oxygen exposure causes the conductance to drop. The next period raises the conductance, whereas all subsequent periods lower the conductance. The diffraction pattern made from the freshly deposited surface [see Fig. 3(a)] shows an fcc structure with a (111) texture. The RHEED patterns taken after several oxidation exposures [see Fig. 3(b)] show a blurring of the fcc (111) texture, indicating the formation of an amorphous oxide. After approximately 300 s of oxygen exposure, a new fcc (111) pattern appears with a larger lattice spacing [see Fig. 3(c)]. This indicates that a layer of CoO is being formed. After 500 s, as seen in Fig. 3(d), the new diffraction pattern has totally replaced the old one. The Co-to-Co atomic spacing of 0.29 ± 0.01 nm measured from the CoO diffraction pattern compares well with

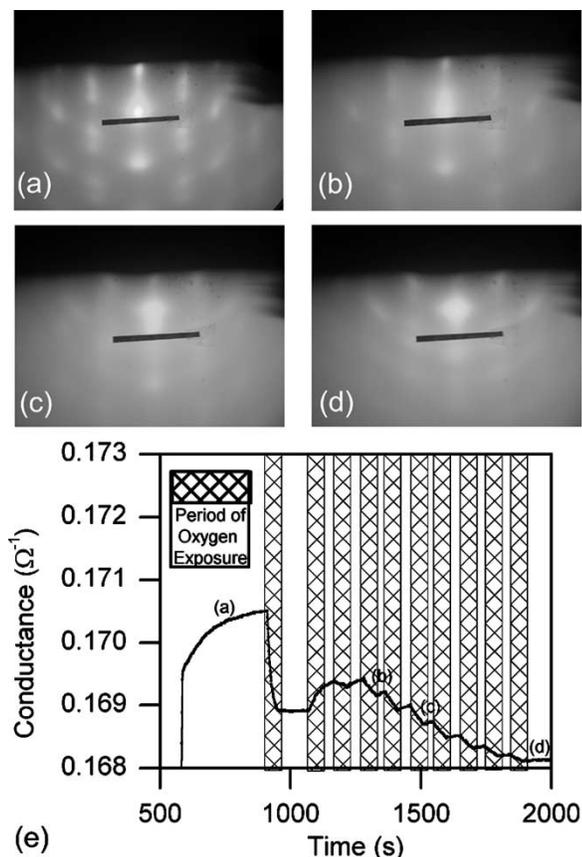


Fig. 3. (a)–(d) RHEED patterns during exposure of a Co surface to oxygen. (e) Conductance as a function of time for this sample as the oxygen flow is turned off and on to allow for the RHEED images to be recorded. The RHEED images in (a)–(d) were taken at the corresponding positions marked in (e). A clear fcc (111) texture is observed in (a) with no oxygen exposure. After 200 s of oxygen exposure (b), the pattern is less distinct, indicating a disordered surface. After 300 s total of oxygen exposure (c), a new fcc crystal lattice with a larger lattice spacing starts to superimpose onto the original diffraction pattern, indicating the formation of CoO. With a total of 500 s of oxygen exposure, the CoO diffraction pattern has totally replaced the original one.

the known atomic spacing of 0.301 nm for CoO [10]. The large difference between the lattice spacing in Co and CoO means that there is probably a thin amorphous layer between the two crystals.

The increase in conductance seen with oxygen exposure occurs before the formation of the CoO layer. This means that the interface between the unorganized oxide that initially forms and

metal has a higher specularity than the metal-vacuum interface. In addition, no change in the response of the conductance to oxygen is seen as the CoO layer appears. This means that the electronic properties of the interface between the Co and the disorganized layer between the Co and the CoO must be similar to the interface between the metal and the initially formed oxide. This would be the case if the amorphous layer between the Co and the CoO were an amorphous oxide.

IV. CONCLUSION

To summarize, a thin amorphous Co oxide layer has a specular interface with the Co layer on which it is grown. It does not appear as if the specularity changes when a CoO crystal forms on top of or replaces the amorphous oxide layer. Self-annealing is observed in samples when no oxygen is present and may play a significant role in the evolution of the oxide at these oxygen pressures.

REFERENCES

- [1] H. J. M. Swagten, G. J. Strijkers, P. J. H. Bloemen, M. M. H. Willekens, and W. J. M. de Jonge, "Enhanced giant magnetoresistance in spin-valves sandwiched between insulating NiO," *Phys. Rev. B.*, vol. 53, pp. 9108–9114, Apr. 1996.
- [2] W. F. Egelhoff *et al.*, "Magnetoresistance values exceeding 21% in symmetric spin valves," *J. Appl. Phys.*, vol. 78, pp. 273–277, July 1995.
- [3] T. C. Anthony, J. A. Brug, and S. Zhang, "Magnetoresistance of symmetric spin valve structures," *IEEE Trans. Magn.*, vol. 30, pp. 3819–3821, Nov. 1994.
- [4] J. Hong, K. Noma, E. Kanda, and H. Kanai, "Very large giant magnetoresistance of spin valves with specularly reflective oxide layers," *Appl. Phys. Lett.*, vol. 83, pp. 960–962, Aug. 2003.
- [5] Y. Kamiguchi, H. Yuasa, H. Fukuzawa, K. Kouji, H. Iwasaki, and M. Sahashi, "CoFe specular spin valves with a nano oxide layer," in Proc. IEEE Int. Magn. Conf., Kyungju, Korea, 1999, Paper DB-01.
- [6] M. F. Gillies, A. E. T. Kuiper, and G. W. R. Leibbrandt, "Effect of thin oxide layers incorporated in spin valve structures," *J. Appl. Phys.*, vol. 89, pp. 6922–6924, June 2001.
- [7] L. J. van der Pauw, "A method of measuring the resistivity and Hall coefficient on lamellae of arbitrary shape," *Philips Tech. Rev.*, vol. 20, pp. 220–224, 1958.
- [8] W. E. Bailey, S. X. Wang, and E. Y. Tsymal, "Electron scattering from Co/Cu interfaces: in situ measurement, comparison with microstructure, and failure of semiclassical free-electron models," *J. Appl. Phys.*, vol. 87, pp. 5185–5187, May 2000.
- [9] B. Dieny, "Classical theory of giant magnetoresistance in spinvalve multilayers: influence of thickness, number of periods, bulk and interfacial spin-dependent scattering," *J. Phys. Condens. Matter*, vol. 4, pp. 8009–8020, 1992.
- [10] *CRC Handbook of Chemistry and Physics*, 83rd ed., D. R. Lide, Ed., CRC, Boca Raton, FL, 2002, pp. 4–21.